Calculation of isotropic hyperfine coupling constants by the symmetry adapted cluster expansion configuration interaction theory

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The isotropic hyperfine coupling constants (HFCCs) are calculated for $H_2O^{+\cdot}$, $CH_2O^{+\cdot}$, $CH_3O^{\cdot}$, $CH_3NH^{\cdot}$, $CH_3CH_2^{\cdot}$, and $CH_3OCH_3^{+\cdot}$, using the method of SAC (symmetry adapted cluster expansion)-CI. After examining various basis sets, we found that the double-zeta quality basis sets of Dunning are the best among the sets examined. The calculated values agree fairly well with the experimental values. We point out that the conventional configuration selection based on the energy criterion has an inherent limit for the calculation of HFCCs. The influence of molecular vibrations on the HFCCs has been semiquantitatively examined for $CH_2O^{+\cdot}$, $CH_3O^{\cdot}$, $CH_3NH^{\cdot}$, and $CH_3CH_2^{\cdot}$.

I. INTRODUCTION

The isotropic hyperfine coupling constant (the Fermi interaction constant) is one of the important physical quantities of open shell molecules. It gives direct information about the unpaired electron spin distribution in the molecules. The hyperfine coupling constant (HFCC) of molecules can be determined experimentally by ESR as well as by microwave spectroscopy. The high resolution microwave spectroscopic technique of transient molecules has recently progressed to the point that a determination of the HFCCs of several polyatomic radicals in the gas phase is possible.[1]

On the other hand, the reliable prediction of HFCCs by *ab initio* MO calculations still remains a challenging problem. Since the HFCC, proportional to the spin density at a nucleus,[2] is a local property of molecules to be described by an operator of delta-function-type, it is a more cumbersome task to calculate them accurately enough by conventional *ab initio* methods than it is to calculate other properties such as the geometry and the energy.[3] In general, large basis sets and an appropriate treatment of electron correlations are indispensable when an ordinary CI approach is adopted in combination with operators of the delta-function-type and basis sets of GTO. In an attempt to deal with this difficult problem the present authors (T.M. and T.S.) proposed replacing the delta-function-type operator with a spatially distributed operator.[4] So far this approach has been explored to the extent that most fundamental problems have been resolved but not to the extent that an immediate application to realistic molecules is yet possible. Therefore, in this work we employed the symmetry adapted cluster expansion configuration interaction (SAC-CI) method developed by one of the present authors (H.N.)[5,6] which has been shown to be efficient in getting favorable results in conjunction with the conventional delta-function-type operator.[7] Emphatically, the SAC and SAC-CI theories attack the entangling problems of the spin correlation, the electron correlation and their coupling in a very rational, and therefore, economical way.[7] In the present study, we demonstrate the capability of the SAC and SAC-CI theories in the calculations of HFCCs of fairly large radicals of interest to chemists.

Compared with the conventional CI method, computations by the SAC-CI method converge rapidly with a small number of variables. The SAC-CI theory satisfies important requirements such as orthogonality and Hamiltonian orthogonality to be imposed upon various states under consideration and the ground state correlation is efficiently utilized for the treatment of the correlation in excited and ionized states. The size of matrices to be diagonalized is determined by the number of linked terms, and a sufficient number of reference configurations can be taken into account without increasing the size of the matrices. Since there are many configurations which contribute negligibly to the total energy, but significantly to the spin density, a conventional perturbation theoretic configuration selection based on the energy criterion is likely to fail. For example, a 1*s* inner shell orbital with a large exponent may be quite significant even if it contributes negligibly to an improvement in the energy. Because of the compactness of the matrices to be diagonalized in the SAC-CI method, it can be applied, without configuration selection, to larger molecules than the usual CI method.

The HFCCs have been observed by ESR spectroscopy for a vast number of molecules. However, most of them are too large for comparison with rigorous calculations. Recently, Engels *et al.* showed that a quite flexible AO basis set like a (12*s*7*p*) Gaussian set or a (13*s*8*p*) set contracted to [8*s*4*p*] is necessary to reproduce satisfactorily the HFCC of the nitrogen atom in the ^4S state.[8] Such a large basis set is obviously not applicable to polyatomic molecules. The main purpose of the present study is to show the capability of the SAC-CI theory to predict HFCCs for various polyatomic molecules with a medium-sized basis set.

In Sec. II we briefly describe the SAC-CI method of calculation. In Sec. III we calculate the HFCCs of $H_2O^{+\cdot}$ as a case study using basis sets of various degrees of sophistication. In Sec. IV through VI we present results for several

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molecules. The influence of molecular vibrations upon HFCCs is discussed semiquantitatively. Finally in Sec. VII, we discuss the HFCCs of the radical cation of dimethyl ether, which was first observed by us,[9] and stimulated our interest in the theoretical reproduction of HFCCs.

II. CALCULATIONAL METHOD

In the present study we have employed method 2 of Ref. 7 to construct the wave function of doublet molecules having a single odd electron. We review the method briefly here. Consider, for example, $H_2O^{+\cdot}$. The first step is to calculate the SAC wave function of the closed-shell molecule, e.g., H_2O, which is constructed by adding a single electron to the doublet molecule of interest, i.e., $H_2O^{+\cdot}$.[5] Then, we construct the doublet wave function for $H_2O^{+\cdot}$ using ionization operators in the SAC-CI theory.[6] Method 2 is more efficient and convenient than method 1 in Ref. 7, which constructs the SAC wave function directly for doublet molecules. The SAC85 program[10] has been used for the calculations.

The threshold of configuration selection for the SAC-CI method was set equal to 0.0 a.u. whereas that of the SAC method was set to 1.0×10^{-5} a.u.[11] That is to say, we did the configuration selection at the stage of the SAC calculation, but not in the SAC-CI calculation. To calculate the HFCC, the spin density matrix has to be constructed. In the unlinked term we included only those SAC operators whose coefficients were larger than 1.0×10^{-3} a.u.[12]

III. $H_2O^{+\cdot}$

The radical cation of water is suitable for testing the basis set dependence of the HFCC since the molecule is small enough to perform *ab initio* calculations with various basis sets, and since the HFCCs of both oxygen and hydrogen atoms were observed by matrix isolation ESR spectroscopy at 4 K.[13] Moreover, an experimentally determined geometry is available.[14]

Table I shows the calculated HFCCs and the total energies for several basis sets of double-zeta (DZ) and even-tempered qualities, both contracted and uncontracted. First, we have compared three DZ sets: Huzinaga's,[15] Dunning's,[16] and Ellinger's[17] (entries 1–3 of Table I). As for Huzinaga's DZ set (entry 1), we split the valence (outermost) basis function of his (73/7) set to a (6121/61) DZ set to increase the flexibility.[15] Dunning's (entry 2) and Ellinger's (entry 3) DZ sets are both contracted from Huzinaga's (9*s*5*p*) primitive.[18] Ellinger's contraction has a larger flexibility in the inner shell orbitals than Dunning's. Huzinaga's primitive hydrogen (4*s*) set was contracted to [2*s*] by the scheme determined by Dunning as [3,1],[16] and was used for the DZ sets Huzinaga (entry 1) and Dunning (entry 2), whereas the contraction scheme determined by Ellinger as [2,2][17] was used for Ellinger's DZ set (entry 3). Next, we proceeded to Huzinaga's primitive (9*s*5*p*/4*s*) set (entry 4) in order to check the effect of the various contractions. A scale factor of 1.2 was used in the primitive for the hydrogen atom in the above four entries. Finally, as an even more flexible basis set, the uncontracted (10*s*5*p*/8*s*) even-tempered Gaussian (ETG) set[19] (entry 6) was used in conjunction with the same set after the contraction to a [8*s*4*p*/6*s*] (entry 5). The contraction scheme was the same as described by Feller and Davidson,[20] i.e., the single *s* and *p* contracted basis functions on each atom were obtained from the inner part of the 1*s* and 2*p* atomic self-consistent field (SCF) orbitals.[21] The contraction from (10*s*5*p*) to [8*s*4*p*] can be denoted alternatively as [31111111/2111]. The exponents and the coefficients of the contracted set are listed in Table II. The ETG set was chosen as a flexible basis set because any orbital with larger exponents can be added systematically in the inner shell according to the prescription given in Ref. 19.

TABLE I. The isotropic hyperfine coupling constant and the total energy of $H_2O^{+\cdot}$ using the SAC-CI calculation.

Basis set	HFCCs(G) O	HFCCs(G) H	Total energy (a.u.)
1. Huzinaga[a] (10*s*7*p*/4*s*)/[4*s*2*p*/2*s*]	−11.74	−26.46	−75.841 360
2. Dunning[b] (9*s*5*p*/4*s*)/[4*s*2*p*/2*s*]	−23.10	−26.16	−75.867 959
3. Ellinger[c] (9*s*5*p*/4*s*)/[4*s*2*p*/2*s*]	−1.97	−26.20	−75.855 172
4. Huzinaga[d] (9*s*5*p*/4*s*) primitive	−17.78	−21.00	−75.959 865
5. Even tempered[e] (10*s*5*p*1*d*/8*s*1*p*)/[8*s*4*p*1*d*/6*s*1*p*]	−19.42	−20.32	−76.095 723
6. Even tempered[f] (10*s*5*p*1*d*/8*s*1*p*) primitive	−19.04	−20.09	−76.111 948
7. Even tempered[g] (11*s*5*p*1*d*/9*s*1*p*) primitive	−19.45	−20.44	−76.113 713
Expt.[h]	29.7	26.1	

[a] Reference 15. Contraction of the oxygen atom can be denoted as [6,1,2,1/6,1]. The basis sets of the hydrogen atom are Huzinaga–Dunning's (4*s*)/[2*s*] with a scale factor of 1.2.
[b] Reference 16.
[c] Reference 17.
[d] Reference 18.
[e] Reference 19. Contraction of the oxygen atom can be denoted as [3,1,1,1,1,1,1,1/2,1,1,1]. Contraction of the hydrogen atom is [3,1,1,1,1,1]. The exponent of a *d* function on the oxygen atom is 0.85. The exponent of a *p* function on the hydrogen atom is 1.2.
[f] Reference 19.
[g] Reference 19. This basis set is essentially the same as 6 except that *s* functions with exponents of 22 788.241 0 and 370.084 67 are added to the oxygen atom and the hydrogen atom, respectively.
[h] Reference 13. The signs cannot be determined.

TABLE II. Exponents and contraction coefficients of the even-tempered basis set (10*s*5*p*/8*s*)/[8*s*4*p*/6*s*].[a]

		Exponent	Coefficient
Oxygen	*s*	7376.100 4	0.074 521 999
		2387.497 0	0.170 063 72
		772.785 31	0.817 881 76
Oxygen	*p*	30.438 774	0.182 527 63
		8.904 834 9	0.873 173 67
Hydrogen	*s*	130.141 49	0.094 983 385
		45.764 686	0.159 235 99
		16.093 303	0.808 195 52

[a] Only contracted orbitals are listed. The uncontracted orbitals of which coefficients are 1.0 are omitted. The SCF energies of the oxygen atom were −74.796 929 a.u. for (10*s*5*p*) primitive ETG set and −74.796 928 a.u. for the [8*s*4*p*] contracted ETG set. The SCF energies of the hydrogen atom were −0.499 974 29 a.u. for both (8*s*) primitive and [6*s*] contracted ETG sets.

Since *s*-type orbitals with large exponents play a crucial role in the calculation of spin density at a nucleus, we also tested a primitive (11*s*5*p*/9*s*) ETG set (entry 7) which was identical with the (10*s*5*p*/8*s*) ETG set except that *s* orbitals with exponents 22 788.241 0 ($=0.093\,108\times3.089\,47^{11}$) and 370.084 67 ($=0.030\,432\,2\times2.843\,71^{9}$) were added to the inner shell of the oxygen atom and the hydrogen atom, respectively. In all the ETG sets (entries 5–7) we added a *d* function on oxygen and a *p* function on hydrogen as the polarization function. The exponents were 0.85 and 1.2, respectively. All six components of the Cartesian *d* function were used.

In all the entries 1–3 the HFCC of the hydrogen remains almost the same and close to the experimental value. The calculated values in these entries are better than that of the (9*s*5*p*) primitive (entry 4) although the latter gives a slightly better total energy than the former three. On the other hand, the calculated HFCC of the oxygen depends sensitively on the contraction scheme for the DZ quality basis sets (entries 1–3), which is inevitable for this class of basis set to describe the first row atoms. However, it should be noted that the HFCC of the oxygen in entry 2 is fairly close to the experimental value.

Even among the ETG sets a comparison of entries 5 and 6 reveals that the contraction produces an improvement in the HFCCs. Since contractions can be regarded as a restriction to inner orbitals with large exponents, and since the coefficients of such orbitals in the contraction scheme may become larger than those obtained by the calculation based on their primitives, contracted basis sets may give larger spin densities than uncontracted ones, which results in better agreement with the experimental HFCCs. It is seen that the (11*s*5*p*1*d*/9*s*1*p*) ETG set (entry 7) shows approach of HFCCs to the experimental values as compared with (10*s*5*p*1*d*/8*s*1*p*) ETG set (entry 6). This tendency of the approach indicates the importance of *s*-type orbitals with large exponents for the calculation of HFCCs. Obviously, cuspless GTOs are an inherently inappropriate choice for a basis set. This problem has been discussed in our previous paper.[4]

All of the three ETG sets (entries 5–7) gave slowly converging HFCCs for both oxygen and hydrogen, but they are still far from the experimental values. However, Table I shows that Dunning's DZ set (entry 2) gives the best agreement with the experimental values despite its DZ quality. We suggest that the contraction in Dunning's DZ set (entry 2) compensates for the deficiency of the uncontracted basis sets for the reason given in the above paragraph and that Dunning's DZ set works well in the vicinity of nuclei. The usefulness of Dunning's DZ set for $H_2O^{+\cdot}$ is important to bear in mind when we proceed to calculate HFCCs of sizable polyatomic molecules (see, e.g., Sec. VIII).

IV. $CH_3O^{\cdot}$, $H_2CO^{+\cdot}$, AND $CH_3NH^{\cdot}$

The r_s structure of the methoxy radical ($CH_3O^{\cdot}$) and its hyperfine coupling constants have recently been determined experimentally by one of the present authors using submillimeter-wave spectroscopy in the gaseous phase.[22] The experimentally determined C–O length lies between the calculated values by Bent *et al.*[23] and by Saebo *et al.*,[25] as shown in Table III. It is noteworthy that, compared with methanol, the experiment found that the methoxy radical had a shorter C–O length and a longer C–H as well as a larger O–C–H angle.

Since no experimental data for the geometry were available for the other two radicals, we employed optimized geometries for these radicals. The geometry of $H_2CO^{+\cdot}$ has been theoretically investigated by Feller and Davidson[27] which is used in the present work. The geometry of $CH_3NH^{\cdot}$ has not been calculated to our knowledge. We determined it by using the UHF approximation with 6-31G* basis sets because the experimentally determined geometry of $CH_3O^{\cdot}$ was fairly well reproduced by this approximation.[25] The optimized parameters are $r(NC) = 1.4457$ Å, $r(NH) = 1.011$ Å, $r(CH_1) = 1.082$ Å, $r(CH_2) = r(CH_3) = 1.089$ Å, $\angle HNC = 107.5°$, $\angle H_1CN = 110.0°$, $\angle H_2CN = \angle H_3CN = 111.1°$, and $\angle H_1CH_2 = 108.6°$. (The dihedral angle between H_1CN and CNH was fixed to 180.0°.)

Since the methyl groups of the methoxy radical and the methylamino radical rotate almost freely under the experimental conditions, the HFCCs of the hydrogens in the methyl group were averaged for the three protons. The methoxy radical with the C_{3v} symmetry, however, was treated as belonging to the C_s symmetry group because of the restriction in the program systems employed[10] so that the electronic

TABLE III. The structure of the methoxy radical in comparison with the structure of methanol.

			r(C–O)	*r*(C–H)	∠HCO
	Expt.[a]		1.3926	1.1177	113.9
$CH_3O^{\cdot}$	Calc.	Bent *et al.*[b]	1.405	1.08[c]	109[c]
		Saebo *et al.*[d]	1.386	1.087	109.9
CH_3OH	Expt.[e]		1.4246	1.0936	108.5

[a] Reference 22.
[b] Reference 23.
[c] Fixed to the values of Yarkony *et al.* (Ref. 24).
[d] Reference 25.
[e] Reference 26.

TABLE IV. HFCCs of $CH_3O^{\cdot}$, $H_2CO^{+\cdot}$, and $CH_3NH^{\cdot}$ using Dunning's DZ sets (in units of Gauss).

	Nucleus	HFCCs	Expt.
$CH_3O^{\cdot}$	O	− 10.56	···
	C	− 15.02	− 15.56[a]
	H	36.57	43.67
$H_2CO^{+\cdot}$	O	− 13.27	···
	C	− 28.92	− 38.8[b]
	H	117.11	132.7
$CH_3NH^{\cdot}$	C	− 11.93	···
	H_{methyl}	29.01	34[c]
	N	6.69	13
	H_N	− 21.47	22

[a] Reference 22.
[b] Reference 28.
[c] Reference 29. The signs cannot be determined.

structure was of either A' or A'' symmetry. Of course, the calculated results for both A' and A'' symmetries were found to be identical.

Table IV shows the result of calculations for HFCCs using Dunning's DZ set without any modifications. The usefulness of Dunning's DZ set was illustrated in the previous section, and the results of a more detailed examination to confirm its usefulness are also given in Sec. VI. All the calculated values are in fair agreement with the experimental values available. It is noteworthy that the HFCCs of the protons, whether they are of the type of alpha or beta, are within 15% of the experimental values. Such an accuracy has not been obtained easily for molecules of this size. This is considered as a consequence of the fact that the SAC-CI method takes into account the electron correlation properly and can include the configurations which contribute significantly to the HFCC, and as a consequence of our finding the appropriateness of Dunning's DZ set. Since the HFCCs of the radical cation of formaldehyde can be reproduced with a quality similar to that of the two other neutral radicals, the charge seems to have no specific effect.

In the calculations argued above, we ignored any dynamical effect such as the molecular vibration. Such a dynamical effect is discussed briefly in Sec. V.

Since the spin density and the total energy are independent quantities, the effect of the conventional configuration selection in CI calculations should be examined. Table V shows the relation between the threshold of selection and the HFCCs for the methoxy radical which was calculated using Dunning's DZ set. The HFCC of oxygen was very sensitive to the selection threshold. The HFCC of the carbon atom did not converge even at a threshold of 10^{-8} a.u. The HFCC of the proton also showed an overall increase with the decrease of the threshold. Thus, configuration selection is not recommended in the calculation of HFCCs. All the calculations of the present study were performed without any configuration selection.

V. INFLUENCE OF MOLECULAR VIBRATIONS

In order to compare the calculated HFCCs with experimental ones, dynamical effects such as molecular vibrations should be taken into account properly. In this section we treat this problem. Although the potential curves for each normal vibration should be drawn to assess the effect of molecular vibrations, such calculations are obviously not practicable for large polyatomic molecules. Therefore, we estimated the effects by varying some geometrical parameters of the radicals along the vibrational modes which are considered to affect the HFCCs most sensitively.

Table VI shows the results of calculations for the three radicals studied. The vibration which changes the angle H–C–O of the methoxy radical is considered to have the largest effect upon the HFCCs. It was found that the HFCC of the proton increases with the angle. According to the total energies calculated by the SAC-CI method, the radical tends to become stabilized slightly as the angle decreases. Thus, the HFCC of the hydrogens may decrease slightly when vibrational averaging is carried out.

As shown in Table VI the total energy of the radical cation of formaldehyde increases steeply as the H–C–O angle changes by − 5°, whereas the HFCCs of the hydrogens increase as the angle changes by + 5°. Therefore, the HFCCs of the hydrogens will become larger when vibrational averaging is taken into account.

The HFCCs of the nitrogen and the hydrogen bonded to the nitrogen in the methylamino radical are not sensitive to vibrations. The HFCC of the hydrogens of the methyl group increase when the H–C–N angle increases. The tendency is the same as with the other radicals.

VI. $CH_3CH_2^{\cdot}$

For the ethyl radical the HFCCs of all the nuclei are determined experimentally,[30] so we will discuss this radical

TABLE V. Effect of the configuration selection threshold in determining the HFCC of $CH_3O^{\cdot}$.

	Threshold of configuration selection (a.u.)[a]				
	10^{-5}	10^{-6}	10^{-7}	10^{-8}	0.0
O	− 37.13	− 7.83	− 6.50	− 10.15	− 10.56
C	− 19.94	− 20.09	− 18.19	− 15.30	− 15.02
H	35.28	36.11	36.45	36.09	36.57
Number of linked configurations[b]	191	300	417	488	808

[a] Threshold for SAC-CI. Threshold for SAC was set to be 1.0×10^{-5} a.u.
[b] Total number of linked configurations was 808.

TABLE VI. Vibrational effects in $CH_3O^{\cdot}$, $CH_2O^{+\cdot}$, and $CH_3NH^{\cdot}$

			HFCCs(G)				Energy differences
			O	C	H		(10^{-3} a.u.)
$CH_3O^{\cdot}$	∠HCO	+ 5°	− 10.75	− 16.22	39.54		6.777
		0°	− 10.56	− 15.02	36.57		0.0
		− 5°	− 10.97	− 13.51	34.34		− 0.457
	Expt.		···	− 15.56	43.67		
$CH_2O^{+\cdot}$	∠HCO	+ 5°	− 13.23	− 30.56	127.08		1.056
		0°	− 13.28	− 28.92	117.12		0.0
		− 5°	− 13.66	− 27.74	109.02		6.691
	Expt.		···	− 38.8	132.7		
			N	C	H_N	H_C	(10^{-3} a.u.)
$CH_3NH^{\cdot}$	$\angle H_C CN$	+ 5°	6.75	− 13.09	− 21.06	34.43	9.344
		0°	6.69	− 11.93	− 21.47	29.01	0.0
		− 5°	6.74	− 10.57	− 21.51	25.34	8.612
	$\angle H_N NC$	+ 5°	6.94	− 11.72	− 21.38	28.67	0.980
		− 5°	6.37	− 12.20	− 21.22	29.18	1.324
	Expt.		13	···	22	34	

in a little more detail than the other radicals discussed above, although an analysis was done previously by one of the present authors.[7] The calculations for the HFCCs using several DZ quality basis sets have been carried out for a calculated geometry by Pacansky *et al.*,[31] and the results are summarized in Table VII. Flexible basis sets like ETG sets are too large to be employed for the calculations of such large polyatomic molecules as the ethyl radical. However, some advantages of the use of DZ sets has been discussed for $H_2O^{+\cdot}$ in Sec. III.

Table VII compares the results obtained by using Dunning's, Ellinger's, and Huzinaga's DZ sets, as in the case of $H_2O^{+\cdot}$. In addition, to increase the flexibility of the radical center carbon atom, we contracted the Huzinaga's *p* function into triple-zeta (TZ) sets. They may be denoted as [6121/511]. As the basis set for the hydrogen atom, Huzinaga's (6*s*) sets[32] contracted to [2*s*] were also used. We also examined the effect of polarization functions on the radical center. Several other basis sets were also tested but results are not shown in Table VII because the essential features were more or less similar to those listed in Table VII.

It is apparent that the double zeta quality basis sets without any modification give fair results for the HFCCs. Upon increasing the flexibility of the basis set for the radical center, the HFCC of the carbon atom of the methylene group, denoted C_α in Table VII, decreased away from the experimental value. The HFCC of the alpha protons also decreased sharply when polarization functions were added on the methylene carbon atom. The increase in the flexibility of orbitals on the radical center may have caused an unwanted spreading of the electron spin density. The HFCCs of the carbon atom tend to depend on the basis set more sensitively than those of the hydrogen atoms.

From Table VII, Dunning's DZ set gives the best result

TABLE VII. HFCCs of the ethyl radical, $CH_3CH_2^{\cdot}$ (in units of Gauss).

Basis sets	C_α	C_β	H_α	H_β^g
1. Dunning[a]	22.2	− 12.2	− 23.1	23.9
2. Ellinger[b]	23.6	− 13.0	− 18.2	22.4
3. Huzinaga A[c]	19.5	− 8.8	− 22.3	24.3
4. Huzinaga B[d]	14.8	− 10.0	− 23.4	24.5
5. Huzinaga C[e]	11.8	− 9.6	− 18.8	23.9
Expt.[f]	29.5	13.6	22.4	26.9

[a] Reference 16.
[b] Reference 17.
[c] Reference 15. The contraction for the carbon and the oxygen atoms can be denoted as [6,1,2,1/6,1]. The basis set of the hydrogen atom is Huzinaga–Dunning (4*s*)/[2*s*] with a scale factor of 1.2.
[d] The same basis set as 3 except that the *p* functions on C are contracted into triple-zeta set as [6,1,2,1/5,1,1]. The hydrogen basis sets of Huzinaga's (6*s*)/[2*s*] were used. (Ref. 32) The contraction can be denoted as [4,2].
[e] The same basis set as 4 except that the *d* orbital with exponent 0.6 was added on the C_α atom.
[f] Reference 30. The signs cannot be determined.
[g] The average of the three protons.

TABLE VIII. Vibrational effect in $CH_3CH_2^{\cdot}$.

		HFCCs (G)				Energy differences (10^{-3} a.u.)
		C_α	C_β	H_α	H_β	
$\angle H_\beta C_\beta C_\alpha$	+ 5°	20.83	− 13.23	− 23.37	22.68	10.547
	0°	22.53	− 11.77	− 23.34	23.85	0.0
	− 5°	22.97	− 10.34	− 23.22	24.76	5.767
$\angle C_\beta C_\alpha X$[a]	+ 5°	25.28	− 11.48	− 22.85	23.84	0.391
	− 5°	20.82	− 11.77	− 23.40	23.92	− 0.471
$\angle H_\alpha C_\alpha H_\alpha$	+ 5°	21.85	− 11.71	− 23.33	24.03	3.073
	− 5°	23.27	− 11.81	− 23.29	23.85	− 0.879
Expt.		29.5	13.6	22.4	26.9	

[a] The symbol X denotes a point which is on the line bisecting the angle, $HC_\alpha H$.

among the three DZ sets for HFCCs as in the case of $H_2O^{+\cdot}$ in Sec. III. Dunning's DZ set describes outer shells of the orbitals more flexibly than Ellinger's DZ set which describes inner shells better that the former. Therefore, it is conjectured from Table VII that better HFCCs are obtained if more flexible outer orbitals are used. This result implies that the tails of valence orbitals extending into inner shells, viz., the probability distribution of the valence electrons in the inner shell, are important in the calculation of HFCCs.

Table VIII shows the effect of molecular distortion on the HFCCs. Three vibrational modes affect the HFCCs. The HFCC of the alpha proton is not sensitive to vibrational distortions. The HFCC of the beta protons increases when the H_β–C_β–C_α angle decreases. Thus, the HFCC of the beta protons will approach the experimental value if the vibrational effect is operative. Since the potential barrier of the bending motion of the methylene unit is found to be so flat, the ethyl radical should be deformed with ease along this vibrational mode. This motion will increase the HFCC of the alpha carbon, thereby improving agreement with the experiment.

VII. $CH_3OCH_3^{+\cdot}$

Compared with those of other organic radicals, the beta proton HFCCs of radical cations of simple ethers are strikingly large.[33] They indicate that part of the odd electron on the oxygen atom is delocalized over the alkyl groups.

As a typical example, the radical cation of dimethyl ether was investigated. Since the geometry has not been determined experimentally, we carried out routine calculations using GAUSSIAN 82,[35] and the results are summarized in Table IX. Since the singly occupied MO has a slightly antibonding character for the C–O bond, the C–O bond length in the radical cation is expected to be slightly shorter than the 1.41 Å bond length of the parent molecule.[34]

Table IX shows that the UHF calculation with double-zeta quality basis sets gave a much longer C–O distance than in the neutral molecule contrary to the expectation stated above. When polarization functions were added on the carbon and the oxygen atoms (6-31G* set), the C–O distance decreased, and when the electron correlation was included using the second order Møller–Plessett perturbation calculation (MP2) it, further, became shorter, although it is still a little longer than the experimental value for the neutral molecule. It is empirically known that polarization functions affect the geometry of neutral molecules more critically than the electron correlation. For example, UHF calculations with 6-31G* are sufficient for the geometry of the neutral radical, $CH_3O^{\cdot}$.[25] In contrast, the result in Table IX shows that not only the effect of polarization function but also the effect of the electron correlation are required for the determination of the geometry of the radical cations. One of the reasons for this difference between the neutral and the charged species is that we used the basis sets that were optimized for neutral atoms. For the calculation of ionic molecules, these basis sets may not be appropriate. If we used the basis sets that were optimized for the ionized atoms, the correlation effect may not be so apparent. As the C–O distance calculated by MP2 is still longer than that of the neutral molecule, it seems that convergence has not yet been achieved, since the C–O distance of the cation is expected to be a little shorter than that of the neutral molecule as stated above. However, further calculations are not practicable for such a large molecule as dimethyl ether, so the geometry determined by the MP2 calculation was used for the calculation of HFCCs with the anticipation that the geometry is a tolerable approximation of the optimum geometry for the radical cation. The full geometry was given in Fig. 1. Al-

TABLE IX. Structure of $CH_3OCH_3^{+\cdot}$.

		MIDI4 UHF	6-31G* UHF	6-31G* MP2[a]
$CH_3OCH_3^{+\cdot}$	C–O (Å)	1.512	1.457	1.421
	∠COC (deg)	123.6	120.22	121.35
			6-31G* RHF	Expt.[b]
CH_3OCH_3	C–O (Å)		1.391	1.41
	∠COC (deg)		113.81	111.7

[a] Full excitation was adopted.
[b] Reference 34.

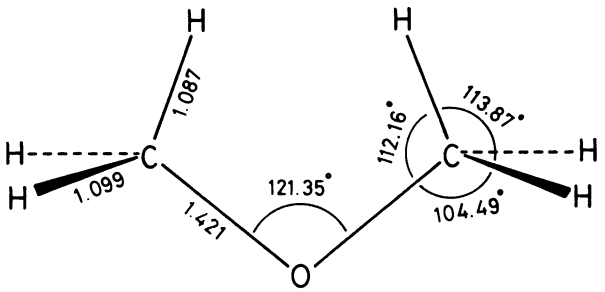

FIG. 1. Optimized geometry of the radical cation of dimethylether.

though there are several combinations for the directions of the methyl groups, the conformation in Fig. 1 was found to be the most stable within the UHF calculation with the double-zeta quality basis set. Actually, since the methyl groups rotate almost freely, the conformation of the methyl group probably does not affect seriously the result of the calculation of HFCCs.

Table X shows the HFCC calculated by the SAC-CI method with Dunning's DZ set in conjunction with the UHF and the annihilated UHF (AUHF), which annihilates the spin contamination in the UHF, calculations. The HFCCs of the beta protons are averaged over the three protons. The calculated value by the SAC-CI method reproduced the large experimental HFCC of beta protons fairly well. It is noticeable that the experimental HFCCs of the protons are much larger than both the UHF and AUHF calculations. It has been found that in other radicals most of the UHF values are larger than the experimental ones, while most AUHF values are smaller.[7] Thus, the case of the radical cations of ethers seems to be peculiar in reference to many other systems so far studied. The reason for this peculiarity is not known and a further investigation should be attempted.

VIII. CONCLUSION

In the present study we have calculated the HFCCs of polyatomic radicals using the SAC-CI method. With Dunning's DZ set, isotropic hyperfine coupling constants have been obtained which are in good agreement with the experimental data, even for fairly large molecules containing beta protons. In particular, the calculated HFCCs of beta protons agree to within 15% with the experimental values. We found that the contracted basis sets gave better results than the primitives, which probably reflects the weakness of the use of unnatural cuspless orbitals as a basis set. The original Dunning contractions of the Huzinaga primitives seem to be suitable for describing the spin density properties at the nuclei.

In conclusion, the important requirements for obtaining reasonably good predictions of HFCCs are, (1) to take into account the electron correlation adequately; (2) to include the configurations which contribute significantly to the HFCC, even if they are not so important for the energy and other properties; and (3) to use basis sets of high quality.

The SAC-CI theory is suited for the calculation of HFCCs, because it takes care of the requirements of (1) and (2) properly. As a result of the rational setup of the theory, the dimensions of matrices to be diagonalized are reduced drastically,[6] so that the SAC-CI method does not require an arbitrary configuration selection. As for the basis set, it is shown that Dunning's DZ set is the best compromise. Since Dunning's DZ set is considered to give an adequate description at and in the vicinity of the nuclei, and since the spin density is a one-electron property just at the nuclei, the adequacy of the set is expected to be transferable from molecule to molecule. This feature is necessary for predicting the spin densities of newly found radicals. Thus, we maintain that the present approach is most useful for the practical treatment of realistic molecules.

TABLE X. HFCCs of $CH_3OCH_3^+$ (in units of Gauss).

	Calc.[a]			
	UHF	AUHF	SAC-CI	Expt.[b]
O	−61.40	−21.15	−16.86	···
C	−17.80	−5.82	−9.29	···
H[c]	30.81	19.43	39.40	43 + 1

[a] Dunning's DZ sets.
[b] Reference 33.
[c] The average of the three protons.

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